

test, a set of the steps of charging at 500 mAh up to 1.2 V followed by resting for 1 hour, then discharging at 500 mAh down to a final discharge voltage of 1.0 V followed by resting for 1 hour is defined as 1 cycle. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 1,000 cycles.

5 Description of Effects of Example 1

[0028] As described later, the capacity reduced to 80% of the initial capacity after 500 cycles in Comparative Example 1 while the capacity reduced to 80% of the initial capacity after 1,000 cycles in Example 1. This means that the adherent property of the electrode to the collector did not reduce in Example 1. Because the oxide film was already formed on the surface of the collector at the time of forming the electrode and the voltage at the time of charge/discharge was lower than the formation voltage, the oxide film was inhibited from further growing in the collector surface. Accordingly, there is no variation in volume of the collector within the charging voltage range. Thus, the adherent property of the electrode to the collector does not reduce and the cyclic property improves.

15 COMPARATIVE EXAMPLE 1

[0029] Comparative Example 1 refers to a method for forming an electrode film without formation of a tantalum plate.

[0030] Comparative Example 1 is a battery producing process having two steps: (1) forming of electrodes; and (2) production of a battery.

20 Operation of Comparative Example 1

[0031] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Comparative Example 1. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 500 cycles. It was also observed that the electrode was peeled off the collector.

25 EXAMPLE 2

[0032] A tantalum plate is employed for a collector and a formed tantalum pentoxide film is disposed on the surface of the tantalum plate. Electrodes formed on collectors are arranged as opposed to each other via an insulating, ion-permeable micro-porous separator. A laminated material surrounds the peripheral portions of the electrodes to hold the electrodes.

[0033] A process for producing a battery according to Example 2 has three steps: (1) formation of tantalum collectors; (2) forming of electrodes; and (3) production of a battery.

35 (1) Formation of tantalum collectors

[0034] A 5-cm square tantalum plate and a SUS plate used for the opposed electrode were immersed into a 0.05-0.6% by weight phosphoric acid (nitric acid or sulfuric acid) solution, and a current of 100 mA/cm² was supplied thereto. The formation voltage was determined to 3 V. The formed tantalum pentoxide film had a thickness of 5 nm and had no transformation color. The oxide film was formed in the range of 70% by area relative to the surface area of the collector.

40 (2) Forming of electrodes

[0035] A mixed powder of PPQx and carbon powder (in a weight ratio of 75:25) for a cathode and a mixed powder of PCI and carbon powder (in a weight ratio of 75:25) for an anode were each mixed with a 20% by weight sulfuric acid aqueous solution to be a paste. They were used to form electrodes in the form of a film on the collectors.

45 (3) Production of a battery

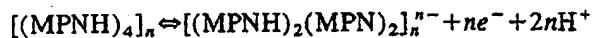
[0036] The thus-formed electrodes were arranged as opposed to each other via a micro-porous separator and their peripheral portions were surrounded by a laminated material to complete a battery.

50 Operation of Example 2

[0037] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Example 2. In this test, a set of the steps of charging at 500 mAh up to 1.2 V followed by resting for 1 hour, then discharging at 500 mAh down to a final discharge voltage of 1.0 V followed by resting for 1 hour is defined as 1 cycle. The test results demonstrate

comparison, we present in Fig. 8(b) the results obtained using HClO_4 (5 mol dm^{-3}) to vary the pH of solutions. At pH values below 2.5, the peak potential E_{pa} shifts by about -0.125 V per pH unit, indicating that two protons per electron are involved in the oxidation and reduction of the polymer.

We have reported elsewhere that the pH sensitivity of unsubstituted polyindole is negligible, compared to the effects observed with poly(5-cyanoindole) [22]. This indicates that the effects of pH are associated with the presence of nitro groups within the films. Kokkinidis and Kelaidopoulou [26] have pointed out that the presence of the nitro $-\text{NO}_2$ group in the 5-position increases the acidity of the indole N-H group so that it can act as a proton donor. We consider that the same influence is possible for the nitro group on the N-H group in the P5NO₂ polymer chain. In order to explain the pH dependence of the electrochemistry of P5NO₂, the deprotonation of the N-H group must be considered as a function of pH and the oxidation state of the polymer. It is reasonable to begin by assuming that all of the N-H groups of the reduced form of the P5NO₂ film are protonated below pH 2.5. By analogy with the parent polyindole [27], it is also assumed that approximately one monomer unit over four can be oxidized. The redox reaction which occurs at pH values below 2.5 can then be represented by the following equation:



where (MPNH) describes the protonated repeat unit in the P5NO₂ chain.

As can be seen from this equation, the loss of one electron is accompanied by the liberation of two protons, i.e., by the deprotonation of two N-H groups. This can produce a -0.118 V per pH unit dependence of the potential upon the pH, which is close to the observed value of about -0.125 V per pH unit.

At pH values above 4.0, all the N-H groups in the oxidized and reduced forms of the polymer are presumably deprotonated. Hence, the potential of the second redox process is independent of the pH of the electrolyte medium.

4. Conclusions

Evidence has been given that 5-nitroindole monomers can lead to the formation of polymer films after oxidative electropolymerization on a platinum electrode in contrast with the results reported by Waltman et al. [16] and in good agreement with our quantum-chemical theoretical calculations reported elsewhere [20]. The polymerization leads to compounds that can be p-doped and which are electroactive. In LiClO_4 /acetonitrile medium, the cyclovoltammograms exhibit only two broad and ill-defined peaks. On transfer to aqueous solutions of HCl or HClO_4 , the P5NO₂ films show two distinct redox processes. The one at lowest potentials occurs over a large potential range, involves electronic exchange only and is insensitive to the pH values. The second

associated with proton exchange and is significantly pH dependent. We have reported elsewhere that there is no pH sensitivity for electrodes coated with polymeric films of the unsubstituted polyindole [22]. Thus, it appears that the pH sensitivity is associated with the presence of the nitro group attached to the polymeric backbone which greatly increases the acidity of the indole N-H group. Then, deprotonation and protonation of the N-H group alternate during the doping and dedoping processes characterized by the exchange of two protons and one electron per monomer unit.

Further work is currently in progress using infrared, in situ spectroelectrochemical and impedance spectroscopies to gain more information about these redox and acid-base reactions.

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that the capacity reduced to 80% of the initial capacity after 2,000 cycles.

Description of Effects of Example 2

5 [0038] While the capacity reduced to 80% of the initial capacity after 1,000 cycles in Example 1, the capacity reduced to 80% of the initial capacity after 2,000 cycles in Example 2. The cyclic property improved in Example 2. This means that the increased formation current enlarged the ratio of the oxide film to the surface area of the collector to improve the adherent property of the electrode to the collector.

10 EXAMPLE 3

[0039] A tantalum plate was employed for a collector and a tantalum pentoxide film formed by gas-phase oxidization was disposed on the surface of the tantalum plate. Electrodes formed on collectors were arranged as opposed to each other via an insulating, ion-permeable micro-porous separator. A laminated material surrounded the peripheral portions 15 of the electrodes to hold the electrodes.

[0040] A process for producing a battery according to Example 3 has three steps: (1) gas-phase oxidization of tantalum collectors; (2) forming of electrodes; and (3) production of a battery.

20 (1) Gas-phase oxidization of tantalum collectors

[0041] A 5-cm square tantalum plate was heated to form a tantalum pentoxide film in air at 400 °C to room temperature for 1 hour or in an oxidative ambient at 200 °C to room temperature for 1 hour. Conditions for the gas-phase oxidization were determined in the following manner. A tantalum plate was heated in air at 400 °C for 1 hour and then in an oxidative ambient at 200 °C for 1 hour to form a tantalum pentoxide film on the tantalum plate. The thickness of the tantalum 25 pentoxide film was measured by a polarization analysis method. The thickness of the tantalum pentoxide film was equal to 5 nm. Thus, the heating conditions were determined as in air at 400 °C to room temperature for 1 hour and in an oxidative ambient at 200 °C to room temperature for 1 hour. No formation color could be observed. The oxide film was formed in the range of 40% by area relative to the surface area of the collector.

30 (2) Forming of electrodes

[0042] A mixed powder of PPQx and carbon powder (in a weight ratio of 75:25) for a cathode and a mixed powder of PCI and carbon powder (in a weight ratio of 75:25) for an anode were each mixed with a 20% by weight sulfuric acid aqueous solution to be a paste. They were used to form electrodes in the form of a film on the collectors.

35 (3) Production of a battery

[0043] The thus-formed electrodes were arranged as opposed to each other via a micro-porous separator and their peripheral portions were surrounded by a laminated material to complete a battery.

40 Operation of Example 3

[0044] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Example 3. In this test, a set of the steps of charging at 500 mAh up to 1.2 V followed by resting for 1 hour, then discharging at 500 mAh down to a final discharge voltage of 1.0 V followed by resting for 1 hour is defined as 1 cycle. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 2,000 cycles.

Description of Effects of Example 3

50 [0045] The collector oxidized in a gas phase in Example 3 also exhibited 2,000 cycles similar to that of a collector treated by formation. The cyclic property improved. This means that the gas-phase oxidization of the collector increased the ratio of the oxide film to the surface area of the collector and improved the adherent property of the electrode to the collector.

55 EXAMPLE 4

[0046] Tantalum plates, once immersed into a hydrofluoric acid solution and then rinsed in water, were oxidized in a gas phase to form electrodes. The electrodes were arranged as opposed to each other via an insulating, ion-perme-

able micro-porous separator. A laminated material surrounded the peripheral portions of the electrodes to hold the electrodes.

[0047] A process for producing a battery according to Example 4 has four steps: (1) etching of tantalum plates, (2) gas-phase oxidization of tantalum collectors; (3) forming of electrodes; and (4) production of a battery.

5 (1) Etching of tantalum plates

[0048] A 5-cm square tantalum plate was immersed into a hydrofluoric acid solution for 10 minutes and then rinsed in water.

10 (2) Gas-phase oxidization of tantalum collectors

[0049] The etched tantalum plate was heated to form an oxide film in air at 400 °C or below for 1 hour or in an oxidative ambient at 200 °C or below for 1 hour. The thickness of the oxide film formed on the surface was equal to 5 nm and no formation color could be observed. The oxide film was formed in the range of 40% by area relative to the surface area of the collector.

15 (3) Forming of electrodes

20 [0050] A mixed powder of PPQx and carbon powder (in a weight ratio of 75:25) for a cathode and a mixed powder of PCl and carbon powder (in a weight ratio of 75:25) for an anode were each mixed with a 20% by weight sulfuric acid aqueous solution to be a paste. They were used to form electrodes in the form of a film on the collectors.

25 (4) Production of a battery

[0051] The thus-formed electrodes were arranged as opposed to each other via a micro-porous separator and their peripheral portions were surrounded by a laminated material to complete a battery.

30 Operation of Example 4

35 [0052] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Example 4. In this test, a set of the steps of charging at 500 mAh up to 1.2 V followed by resting for 1 hour, then discharging at 500 mAh down to a final discharge voltage of 1.0 V followed by resting for 1 hour is defined as 1 cycle. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 4,000 cycles.

40 Description of Effects of Example 4

45 [0053] While the capacity reduced to 80% of the initial capacity after 600 cycles in Comparative Example 2 as described later, the capacity reduced to 80% of the initial capacity after 4,000 cycles in Example 4. This means that the adherent property of the electrode to the collector did not reduce in Example 4. Because the oxide film was already formed on the surface of the collector at the time of forming the electrode and the voltage at the time of charge/discharge was lower than the formation voltage, the oxide film was inhibited from further growing on the collector surface. Accordingly, there is no variation in volume of the collector within the charging voltage range. Thus, the adherent property of the electrode to the collector does not reduce and the cyclic property improves.

50 COMPARATIVE EXAMPLE 2

[0054] Comparative Example 2 refers to a method for forming an electrode in the form of a film without oxidizing a tantalum plate in a gas phase as described in Example 4.

[0055] A process for producing a battery according to Comparative Example 2 has three steps: (1) etching of tantalum plates; (2) forming of electrodes; and (3) production of a battery.

55 Operation of Comparative Example 2

[0056] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Comparative Example 2. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 600 cycles. It was also observed that the electrode was peeled off the collector.

EXAMPLE 5

[0057] A niobium plate was employed for a collector and a niobium pentoxide film formed by formation was disposed on the surface of the niobium plate. Electrodes formed on the collectors were arranged as opposed to each other via an insulating, ion-permeable micro-porous separator. A laminated material surrounded the peripheral portions of the electrodes to hold the electrodes.

[0058] A process for producing a battery according to Example 5 has three steps: (1) formation of niobium collectors; (2) forming of electrodes; and (3) production of a battery.

10 (1) Formation of niobium collectors

[0059] A 5-cm square niobium plate and a SUS plate used for the opposed electrode were immersed into a 0.05-0.6% by weight phosphoric acid (nitric acid or sulfuric acid) solution, and a current of 10 mA/cm^2 was supplied thereto. When the voltage reached up to 3 V, it was held during a holding time of 1 hour. The niobium pentoxide film formed on the surface had a thickness of 7.2 nm and had no formation color. The oxide film was formed in the range of 50% by area relative to the surface area of the collector.

15 (2) Forming of electrodes

20 [0060] A mixed powder of PPQx and carbon powder (in a weight ratio of 75:25) for a cathode and a mixed powder of PCl and carbon powder (in a weight ratio of 75:25) for an anode were each mixed with a 20% by weight sulfuric acid aqueous solution to be a paste. They were used to form electrodes in the form of a film on the collectors.

25 (3) Production of a battery

[0061] The thus-formed electrodes were arranged as opposed to each other via a micro-porous separator and their peripheral portions were surrounded by a laminated material to complete a battery.

Description of Operation of Example 5

30 [0062] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Example 5. In this test, a set of the steps of charging at 500 mAh up to 1.2 V followed by resting for 1 hour, then discharging at 500 mAh down to a final discharge voltage of 1.0 V followed by resting for 1 hour is defined as 1 cycle. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 1,000 cycles.

35 Description of Effect of Example 5

40 [0063] While the capacity reduced to 80% of the initial capacity after 350 cycles in Comparative Example 3 as described later, the capacity reduced to 80% of the initial capacity after 600 cycles in Example 5. This means that the adherent property of the electrode to the collector did not reduce in Example 5. Because the oxide film was already formed on the surface of the collector at the time of forming the electrode and the voltage at the time of charge/discharge was lower than the formation voltage, the oxide film was inhibited from further growing on the collector surface. Accordingly, there is no variation in volume of the collector within the charging voltage range. Thus, the adherent property of the electrode to the collector does not reduce and the cyclic property improves.

45 COMPARATIVE EXAMPLE 3

[0064] Comparative Example 3 refers to a method for forming an electrode in the form of a film without formation of a niobium plate.

50 [0065] A process for producing a battery according to Comparative Example 3 has two steps: (1) forming of electrodes; and (2) production of a battery.

Operation of Comparative Example 3

55 [0066] A charge/discharge cyclic test was performed to check its cyclic property of the battery of Comparative Example 3. The test results demonstrate that the capacity reduced to 80% of the initial capacity after 350 cycles. It was also observed that the electrode was peeled off the collector.

Table 1

	The number of cycles down to 80% of the initial capacity
Example 1	1000
Example 2	2000
Example 3	2000
Example 4	4000
Example 5	1000
Comparative Example 1	500
Comparative Example 2	600
Comparative Example 3	350

[0067] As obvious from the above, first, an oxide film of a thickness of 1.7-10 nm is formed on the surface of a collector made of a valve action metal. The oxide film is formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of the collector. An electrode is formed in the form of a film on the collector.

20 The electrode is used for a secondary battery. The electrode and battery are excellent in cyclic property and film-forming property.

[0068] As the embodiments consistent with the present invention have been described, other embodiments and variations consistent with the invention will be apparent to those skilled in the art. Therefore, the invention should not be viewed as limited to the disclosed embodiments but rather should be viewed as limited only by the spirit and scope 25 of the appended claims.

Claims

30 1. A secondary battery comprising:

a first collector made of a first valve action metal;
 a second collector made of a second valve action metal;
 a first electrode;
 a second electrode;
 a separator; and
 an outer can,

35 wherein said first collector is covered with a first oxide film of a thickness of 1.7-10 nm, said first oxide film being formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of said first collector, said first collector having said first electrode disposed thereon;

40 said second collector is covered with a second oxide film of a thickness of 1.7-10 nm, said second oxide film being formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of said second collector, said second collector having said second electrode disposed thereon.

45 2. The secondary battery of claim 1, wherein said first valve action metal is Ta or Nb.

3. The secondary battery of claim 1, wherein said second valve action metal is Ta or Nb.

4. The secondary battery of claim 1, wherein said first electrode is a mixture comprising polyphenylquinoxaline, carbon powder and a sulfuric acid aqueous solution.

5. The secondary battery of claim 1, wherein said second electrode is a mixture comprising polycyanoindole, carbon powder and a sulfuric acid aqueous solution.

55 6. The secondary battery of claim 1, wherein said separator is a micro-porous separator.

7. The secondary battery of claim 1, wherein said first oxide film is made of tantalum pentoxide or niobium pentoxide.

8. The secondary battery of claim 1, wherein said second oxide film is made of tantalum pentoxide or niobium pentoxide.

5 9. An electrode for a secondary battery which comprises a collector made of a valve action metal and a paste film formed on said collector,
wherein said collector is covered with an oxide film of a thickness of 1.7-10 nm, said oxide film being formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of said collector.

10 10. The electrode of claim 9, wherein said paste film is a mixture comprising polyphenylquinoxaline, carbon powder and a sulfuric acid aqueous solution.

15 11. The electrode of claim 9, wherein said paste film is a mixture comprising polycyanoindole, carbon powder and a sulfuric acid aqueous solution.

12. The electrode of claim 9, wherein said valve action metal is Ta or Nb.

13. The electrode of claim 9, wherein said oxide film is made of tantalum pentoxide or niobium pentoxide.

20 14. A method of producing a secondary battery comprising a first collector made of a first valve action metal, a second collector made of a second valve action metal, a first electrode, a second electrode, a separator and an outer can, wherein said method comprises:
25 forming a first oxide film of a thickness of 1.7-10 nm on said first collector, said first oxide film being formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of said first collector;
forming a second oxide film of a thickness of 1.7-10 nm on said second collector, said second oxide film being formed in a range of 30% or more to less than 100% by area relative to the surface area of said second collector;
forming said first electrode on said first collector; and
forming said second electrode on said second collector.

30 15. The method of claim 14, wherein said first valve action metal is Ta or Nb.

16. The method of claim 14, wherein said second valve action metal is Ta or Nb.

35 17. The method of claim 14, wherein said first electrode is a mixture comprising polyphenylquinoxaline, carbon powder and a sulfuric acid aqueous solution.

18. The method of claim 14, wherein said second electrode is a mixture comprising polycyanoindole, carbon powder and a sulfuric acid aqueous solution.

40 19. The method of claim 14, wherein said separator is a micro-porous separator.

20. The method of claim 14, wherein said first oxide film is made of tantalum pentoxide or niobium pentoxide.

21. The method of claim 14, wherein said second oxide film is made of tantalum pentoxide or niobium pentoxide.

45 22. The method of claim 14, wherein a formation voltage higher than the working voltage of said secondary battery is applied to said first collector to form said first oxide film.

23. The method of claim 22, wherein said formation voltage is 3 V.

50 24. The method of claim 14, wherein a formation voltage higher than the working voltage of said secondary battery is applied to said second collector to form said second oxide film.

25. The method of claim 24, wherein said formation voltage is 3 V.

55 26. A method of producing an electrode for a secondary battery which comprises:
forming an oxide film of a thickness of 1.7-10 nm on a collector made of a valve action metal, said oxide film

being formed in a range of from 30% by area or more to less than 100% by area relative to the surface area of said collector; and
forming a paste film on said collector.

5 27. The method of claim 26, wherein said paste film is a mixture comprising polyphenylquinoxaline, carbon powder and a sulfuric acid aqueous solution.

10 28. The method of claim 26, wherein said paste film is a mixture comprising polycyanoindole, carbon powder and a sulfuric acid aqueous solution.

10 29. The method of claim 26, wherein said valve action metal is Ta or Nb.

15 30. The method of claim 26, wherein said oxide film is made of tantalum pentoxide or niobium pentoxide.

15 31. The method of claim 26, wherein a formation voltage higher than the working voltage of said secondary battery is applied to said collector to form said oxide film.

20 32. The method of claim 31, wherein said formation voltage is 3 V.

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FIG. 1

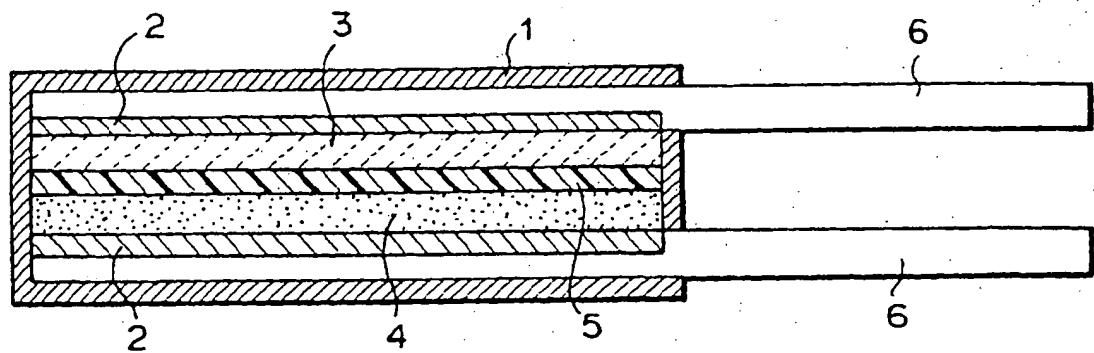


FIG. 2

